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arrived at by dialysing a solution of acetate of alumina that has been altered by heat. In three days the acetic acid was reduced on the dialyser to 11 per cent., giving 1 equiv. acetic acid to 8 equivs. alumina; in six days to 7·17 per cent. acid; in thirteen days to 2·8 per cent. acid, or 1 equiv. acid to 33 equivs. alumina. The alumina exists in an allotropic condition, being no longer a mordant; and forming, when precipitated, a jelly that is not dissolved by an excess of acid. Metalumina resembles alumina in being coagulated by minute proportions of acids, bases, and of most salts. Mr. Crum found the solution of metalumina to require larger quantities of acetates, nitrates, and chlorides to produce coagulation than of sulphates. The solution of metalumina is tasteless, and entirely neutral to test-paper, according to my own observation.

Like alumina, the present colloid has therefore a fluid and a pectous form, the liquid soluble metalumina, and the gelatinous insoluble metalumina.

Soluble Peroxide of Iron.—A solution of hydrated peroxide of iron may be obtained by a process exactly analogous to that for soluble alumina. Perchloride of iron in solution is first saturated with hydrated peroxide of iron, added by small quantities at a time; or carbonate of ammonia may be added in a gradual manner to perchloride of iron, so long as the precipitated oxide continues to be redissolved on stirring. These red solutions of iron have lately been carefully investigated by Mr. Ordway (Silliman's Journal, [3], xxxix. 197), by M. Béchamp (Ann. Ch. Phys. [3], lvii. 293), and by M. Scheurer-Kestner (ibid. lv. 330). It is observed that the act of solution of the hydrated peroxide by the chloride of iron is a gradual process, demanding time. The quantity of oxide taken up will go on increasing for a long period, if digestion in the cold is continued. Mr. Ordway found chloride of iron to take up as much as 18 equivalents of peroxide of iron in the course of five months. This slowness of action is highly characteristic of colloids. Only monobasic acids, such as hydrochloric and nitric, serve for preparing such solutions, sulphuric and other polybasic acids giving insoluble subsalts with excess of ferric oxide, or of any other aluminous oxide. The red liquid so obtained is already a colloidal hydrochlorate of peroxide of iron, but requires to be dialysed for a sufficient time. Such a compound possesses an element of instability in the extremely unequal diffusibility of its constituents. Beginning with perchloride of iron,

containing five or six equivalents of peroxide in solution, the whole solid matter also amounting to 4 or 5 per cent. of the liquid, and the latter forming a stratum of the usual depth of about half an inch in the dialyser, it was found that hydrochloric acid diffused out accompanied only by a small proportion of the iron. After eight days, the deep red solution in the dialyser contained peroxide of iron and hydrochloric acid, in the proportion of 97·6 per cent. of the former to 2·4 per cent. of the latter. In nineteen days the hydrochloric acid was reduced to 1·5 per cent., which gives 1 equiv. of acid to 30·3 equivs. peroxide of iron. The last solution was transferred to a phial, in which it remained fluid for twenty days, and then spontaneously pectized.

The peracetate of iron, prepared by double decomposition, is incapable of dissolving hydrated peroxide of iron, as is well known, but still may be made a source of soluble peroxide; as the salt referred to is itself decomposed to a great extent by diffusion on the dialyser. About one-half of the iron was lost by a diffusion of eighteen days, in a particular experiment, leaving on the dialyser a red liquid, in which ninety-four parts of peroxide of iron were still associated with six parts of acetic acid.

Water containing about 1 per cent. of hydrated peroxide of iron in solution has the dark red colour of venous blood. The solution may be concentrated by boiling to a certain point, and then pectizes. The red solution is coagulated in the cold by traces of sulphuric acid, alkalies, alkaline carbonates, sulphates and neutral salts in general, but not by hydrochloric, nitric, and acetic acids, nor by alcohol or sugar. The coagulum is a deep red-coloured jelly, resembling the clot of blood, but more transparent. Indeed the coagulation of this colloid is highly suggestive of that of blood, from the feeble agencies which suffice to effect the change in question, as well as from the appearance of the product. The coagulum formed by a precipitant, or in the course of time, without any addition having been made to the solution of peroxide of iron, is no longer soluble in water, hot or cold, but it yields readily to dilute acids. It is, in short, the ordinary hydrated peroxide of iron. Here then, again, we have a soluble and insoluble form of the same colloidal substance. Native hematite, which presents itself in mammillary concretions, is no doubt colloidal.

Soluble Metaperoxide of Iron.—The soluble peroxide of iron of M. Péan de Saint-Gilles* appears to be the analogue of meta-

* Comptes rendus, 1855, vol. xl. p. 568.

lumina. It was also prepared by the prolonged action of heat upon a pure solution of the acetate. The characteristic properties of this substance, which indicate its allotropic nature, are the orange-red colour and the opalescent appearance of its solution. The metaperoxide of iron is entirely precipitated of a brown ochreous appearance by a trace of sulphuric acid, or of an alkaline salt, and is insoluble in all cold acids, even when the latter are concentrated. The solubility of metaperoxide of iron in water appears to be more precarious, if possible, than that of the colloid alumina. It would no doubt be more safely prepared by diffusing away the acetic acid of the altered acetate of iron, than it is by boiling off that acid, as the solution is said to become precipitable by heat before the whole acetic acid is expelled.

Ferrocyanide of Copper.—Many of the insoluble ferrocyanides are crystalline precipitates, but the compound above named, and the different varieties of prussian blue, appear to be strictly colloidal.

Certain anomalous properties long observed in these compounds come thus to be explained. The ferrocyanide of copper precipitated from ferrocyanide of potassium and sulphate of copper, is a reddish-brown gelatinous precipitate, and carries down a portion of the potash salt. It is obtained of greater purity, like the other insoluble ferrocyanides, by the use of ferrocyanic acid as the precipitant. Ferrocyanide of copper is then darker in colour, and still more highly gelatinous. It is well known that this substance appears as a transparent almost colourless jelly, when precipitated from strong solutions. This colloidal matter assumes colour on the addition of water, in consequence of further hydration, following in this respect the analogy of the crystalloid salts of copper. The ferrocyanide of copper, when once precipitated, may be washed without loss, and exhibits no symptoms of solubility. But it has been remarked that the same salt, when produced by mixing the precipitating salts dissolved in not less than two or three thousand times their weight of water, gives a wine-red solution with no precipitate. This is the soluble condition of the colloid. When the red solution is placed in the dialyser, the salt of potash diffuses out, and the whole ferrocyanide of copper is retained behind in solution

Precipitated ferrocyanide of copper is not dissolved by oxalic acid, nor by oxalate of potash, but dissolves freely in about one-fourth of its weight of neutral oxalate of ammonia. The ferro-

cyanide of copper must be washed beforehand, to ensure solubility. A solution holding 3 or 4 per cent. of ferrocyanide of copper is of a dark reddish-brown colour, intermediate in tint between the acetate and meconate of iron. The solution is transparent, but assumes a peculiar appearance of opacity when seen by light reflected from its surface. The same appearance was observed by Péan de Saint-Gilles in his metaperoxide of iron.

When a red solution, such as that described, was dialysed, the oxalate of ammonia came away in a gradual manner; 30·6 per cent. of the oxalate of ammonia was found in the colourless diffusate of the first twenty-four hours, 31 per cent. of the same salt in the diffusate of the next three days, and 18·2 per cent. in the diffusates of the following seven days, making altogether 79·8 per cent., or four-fifths of the whole oxalate of ammonia originally introduced. A small portion of the ammoniacal salt is retained with force, as might be expected from a ferrocyanide. Although the diffusate appeared colourless, it was found to contain a little oxide of copper, namely, 0·041 gramme (of which 0·022 gramme diffused out in the first twenty-four hours), from 2 grammes of ferrocyanide of copper placed in the dialyser.

The liquid ferrocyanide of copper, both before and after being dialysed, may be heated without change, but it is pectized by foreign substances with extreme facility. This effect is produced by a minute addition of nitric, hydrochloric, and sulphuric acids in the cold, and of oxalic and tartaric acids with the aid of a slight heat. It is remarkable that acetic acid does not pectize the ferrocyanide of copper and many other colloids. Sulphate of potash, sulphate of copper, and metallic salts generally appear to pectize the red liquid. The oxalate of ammonia, if any is present, remains in solution.

Neutral Prussian Blue.—The blue precipitate from perchloride of iron and ferrocyanide of potassium, or ferrocyanic acid, is a bulky hydrate, which dries up into gummy masses, so far resembling a colloid. The precipitate dissolves readily with the aid of a gentle heat, in one-sixth of its weight of oxalic acid, giving the well-known solution of prussian blue, used as a blue ink. Prussian blue is equally soluble in the oxalate and binoxalate of potash. When the solution of prussian blue in oxalic acid was placed on the dialyser, no colouring matter came through, but 28 per cent. of the oxalic acid diffused away in the first twenty-four hours, accompanied by traces of peroxide of iron. The oxalic acid appears

to leave the colloidal solution very slowly and incompletely, 8 per cent. diffusing away in the second twenty-four hours, 11 per cent. in the next four days, and 2 per cent. in the following six days. The colloidal solution of prussian blue was pectized by small additions of sulphate of zinc and several other metallic salts, but required larger quantities of the alkaline salts for precipitation.

Ferridcyanide of Iron.—The blue precipitate from the ferridcyanide of potassium and a protosalt of iron is soluble in oxalic acid and binoxalate of potash, but not in the neutral oxalates. This blue liquid is quite incapable of passing through the dialyser, and is equally colloidal with ordinary prussian blue. So also is *basic prussian blue* prepared by the spontaneous oxidation of precipitated ferrocyanide of protoxide of iron. This last colloid might probably be purified with advantage upon the dialyser.

The ammonio-tartrate of iron, ammonio-citrate of iron, and similar pharmaceutical preparations are chiefly colloidal matters.

Sucrate of Copper.—The deep blue liquid obtained by adding potash to a mixed solution of chloride of copper and sugar appears to contain a colloidal substance. Placed on a dialyser for four days, the blue liquid became green, and no longer contained either potassium or chlorine; it, in fact, consisted of oxide of copper united with twice its weight of sugar. The external liquid remained colourless, and gave no indication of copper when tested with sulphuretted hydrogen. The colloidal solution of sucrate of copper was sensitive in the extreme to pectizing agents. Salts and acids generally gave a bluish-green precipitate; even acetic acid had that effect. The precipitate, or pectous sucrate, after being well washed, consisted of oxide of copper with about half its weight of sugar, and is therefore a subsucrate. When the green liquid is heated strongly, it gives a bluish-green precipitate, and does not allow the copper to be readily reduced to the state of suboxide. The subsucrate of copper possesses considerable vivacity of colour, and might be used as a pigment. A solution of sucrate of copper absorbs carbonic acid from the air with great avidity.

The sucrate of copper dries up into transparent films of an emerald-green colour. These films are not altered in appearance or dissolved in cold or boiling alcohol. In water they are resolved into sugar and the pectous subsucrate of copper.

Sucrate of Peroxide of Iron.—The perchloride of iron with an addition of sugar is not precipitated by potash, provided the temperature is not allowed to rise. The peroxide of iron combined

with the sugar is colloidal, and remains on the dialyser without loss. At a certain stage, however, the sugar appears to leave the peroxide of iron, and a gelatinous subsucrate of iron pectizes. The subsucrate of iron thrown down from the soluble sucrate by the addition of sulphate of potash, consisted of about 22 parts of sugar to 78 parts of peroxide of iron.

Sucrate of Peroxide of Uranium.—A similar solution may be obtained by adding potash to a mixture of the nitrate or chloride of uranium with sugar, avoiding heat. The solution is of a deep orange-yellow colour, and on the dialyser soon loses the whole of its acid and alkali. This fluid sucrate has considerable stability, but, like the sucrate of copper, is readily pectized by salts. The subsucrate pectized has considerable solubility in pure water.

Sucrate of Lime.—The well-known solution of lime in sugar forms a solid coagulum when heated. It is probably, at a high temperature, entirely colloidal. The solution obtained on cooling passes through the septum, but requires a much longer time than a true crystalloid like the chloride of calcium.

The blue solution of tartrate of copper in caustic potash contains a colloidal compound which has not been fully examined.

Soluble Chromic Oxide.—The definite terchloride of chromium, being a crystalloid, diffuses away entirely when placed in solution upon the dialyser. This salt, dissolves, with time, a certain portion of freshly precipitated hydrated chromic oxide, and becomes of a deeper green colour. Such a solution, after dialysis for twenty-two days, contained 8 hydrochloric acid to 92 chromic oxide; and after thirty days, 4·3 acid to 95·7 oxide, or 1 equiv. acid to 10·6 equivs. oxide. After thirty-eight days, the solution gelatinized in part upon the dialyser, and then contained 1·5 acid to 98·5 oxide, or 1 equiv. acid to 31·2 equivs. chromic oxide. This last solution, which may be taken to represent soluble chromic oxide, is of a dark green colour, and admits of being heated, and also of being diluted with pure water without change. It was gelatinized with the usual facility by traces of salts and other reagents which affect colloid solutions, and was then no longer soluble in water, even with the assistance of heat. It appeared to be the green hydrated oxide of chromium, as that substance is usually known. A metachromic oxide may possibly be obtained by heating and dialysing the acetate, but I have not attempted to form it.

Mr. Ordway succeeded in dissolving an excess of hydrated *uranic oxide* and of *glucina* in the chloride of uranium and of

glucinum respectively. The dialysis of such solutions may be reasonably expected to yield soluble uranic oxide and soluble glucina.

It appears, then, that the hydrated peroxides of the aluminous type, when free, are colloid bodies; that two species of each of these hydrated oxides exist, of which alumina and metalumina are the types; one derived from an unchanged salt, and the other from the heated acetate of the base; further, that each of these species has two forms, one soluble and the other insoluble, or coagulated. This last species of duality should be well distinguished from the preceding allotropic variability of the same peroxide. The possession of a soluble and an insoluble (fluid and pectous) modification is not confined to hydrated silicic acid and the aluminous oxides, but appears to be very general, if not universal, among colloid substances. The double form is typified in the fibrin of blood.

The precipitated and gelatinous *peroxide of tin* is largely soluble in the bichloride of the same metal. Such a solution, when placed in the dialyser, allows the whole chlorine of the salt and a portion of the tin to diffuse away. Peroxide of tin or stannic acid remains behind, but not in a soluble state. It forms in the dialyser a semitransparent gelatinous cake, which after a few days is entirely free from chlorine. The original solution, containing excess of stannic acid, was diluted to various degrees, but was dialysed always with the same result. The coagulum was insoluble in hot or cold water, but dissolved readily in dilute acids. It was evidently the peroxide of tin unaltered.

The *metastannic acid,* or nitric acid peroxide of tin of Berzelius, forms a solid compound with a small quantity of hydrochloric acid. The compound is not dissolved by an excess of acid, but is soluble in pure water. The solution placed in the dialyser is readily decomposed, and leaves behind a semitransparent gelatinous mass of pure hydrated metastannic acid, insoluble both in water and acids. There appears, then, to be no soluble form of either hydrated stannic or metastannic acid, although both are colloidal substances.*

* The soluble stannic and metastannic acids have since been obtained by dissolving the gelatinous substances above referred to in a small proportion of caustic potash; then neutralizing with acetic acid and dialysing again. The stannic or metastannic acid now remains fluid on the dialyser. Some alkali still adhering may be removed by the cautious addition of iodine dissolved in alcohol, the dialysis being continued. Stannic acid remains fluid when heated, but is converted into metastannic acid.—*Note by the Author.*

Precipitated *titanic acid* was dissolved in hydrochloric acid and submitted to dialysis. The hydrochloric acid readily diffused away, leaving hydrated titanic acid, gelatinous and insoluble, upon the dialyser. The proportion of titanic acid, which escaped from the dialyser and was lost, amounted to 0·050 gramme out of 2·5 grammes. Titanic acid thus resembles stannic acid in not presenting itself in the form of a fluid colloid.

Metallic protoxides are not soluble in their neutral salts, and cannot therefore be submitted to dialysis in the same conditions as the preceding peroxides. It was observed, however, that oxide of copper and oxide of zinc, when dissolved in ammonia, are capable of diffusing through a collodial septum, and are therefore not colloids themselves. The water outside the dialyser should be charged with ammonia in such an experiment.

5. *Dialysis of Organic Colloid Substances.*

Tannin.—The tannin employed was that extracted from gall-nuts by the ether process of Pelouze. A two per cent. solution of this substance, covering a surface of paper-parchment of the area of about $\frac{1}{100}$th of a square meter, or 15·6 square inches, to a depth of 10 millimeters, was diffused at 10° to 13° of temperature. The diffused matter amounted, in successive periods of twenty-four hours, to ·073, ·040, ·021, ·021, ·024 and ·024 gramme, derived from the two grammes in solution. Probably the earlier diffusates were increased by the presence of a little gallic acid, which, being a crystalloid, would no doubt be rapidly eliminated by diffusion. The latter observations indicate that tannin passes through a paper-parchment septum about 200 times less rapidly than chloride of sodium does in similar circumstances as to temperature and strength of solution. The diffusates from the tannin solution gave a precipitate with gelatin, and therefore contained tannin unaltered. But the diffusates probably contained also throughout some products of decomposition of a crystalloid character.

To the low diffusibility of tannin may be ascribed the remarkably slow penetration of skins by that substance in the ordinary operation of tanning leather. Tannin appears to form compounds of much stability with certain other colloids, as tanno-gelatin, and the compound with albumin which appears to be the primary basis of the vegetable cell (Fremy).

Gum. — The diffusate obtained from a solution containing 2 grammes of gum-arabic, in experiments corresponding in their conditions with the experiments upon tannin just related, was ·013 gramme per day. The power of gum to penetrate the colloid septum appears, therefore, to be one-half less than that of tannin, and 400 times less than the diffusibility of chloride of sodium. Gum gave the same amount of diffusate with a mucous septum as with parchment-paper. When substances of the crystalloid class are mixed with the gum, the diffusion of the latter appears to be still further reduced, and may even be entirely extinguished. The separation of colloids from crystalloids by dialysis is, in consequence, generally more complete than might be expected from the relative diffusibility of the two classes of substances.

Vegetable gum, which Fremy has shown to be a gummate of lime, can be purified by a dialytic method, which may be found applicable with advantage in other cases. Oxalic acid, it is known, precipitates lime from the gum very imperfectly. Hydrochloric acid may be used to separate that base from a solution of gum placed upon the dialyser, with more effect. It is only necessary to add to a strong solution of gum 4 or 5 per cent. of hydrochloric acid, and to dialyse till the gum-solution gives no precipitate with nitrate of silver. In an experiment made upon a 20 per cent. solution of gum, the ash was reduced to 0·1 per cent. of the gum in five days. The gummic acid possesses a sensible acid reaction, about equal to that of carbonic acid. This acid reaction was neutralized, in 100 parts of gummic acid, by 2·85 parts of potash. This amount of potash is very nearly equivalent to the lime originally present in the gum (1·72 lime, or 3·07 carbonate of lime, being equivalent to 2·89 potash). When the gummate of potash itself was dialysed without addition, the potash gradually diffused away, possibly in the state of carbonate, and left the gum again possessed of an acid reaction. Gummic acid, well dried at 100°, becomes insoluble in water, but swells up in that liquid, like gum-tragacanth. We appear to have here the pectous form of gummic acid.

It is worthy of inquiry whether such native gums as are insoluble in water are not the pectous forms of soluble gum, rather than allotropic varieties of that substance. So also of the metagummic acid of Fremy, formed by the action of strong sulphuric acid on mucilage. This last substance is insoluble in water, but was found by Fremy to afford, when neutralized by

lime and alkalies, a soluble gum undistinguishable from gum-arabic.

Gummic acid produces a remarkable compound with gelatine. When solutions of these two colloids are mixed, oily drops fall and form a nearly colourless jelly on standing. This jelly is very fusible, melting at 25°, or by the heat of the hand. The *gummate of gelatin* may be washed slightly without decomposition, but is soluble to a certain extent in pure water, and still more so in a solution of gelatine. Prepared with gummic acid in excess, the compound, when dried at 100°, consisted of 100 gummic acid with 59 gelatin. The drops and the jelly contained 83·5 per cent. of water. Solution of gelatin is not precipitated by unpurified gum, nor by the gummate of potash.

Dextrin.—A two per cent. solution of dextrin, prepared from starch, was diffused in the same conditions as the preceding substances, but through a mucus septum. It gave in twenty-four hours ·034 gramme of diffusate from 2 grammes, or about three times more diffusate than was given by gum-arabic.

Caramel.—The dialytic examination of this substance adds to the accurate information on the subject lately supplied by M. A. Gélis*, and places caramel indisputably in the colloid class. The crude caramel obtained by heating cane-sugar at 210°—220°, when placed on the dialyser, allows certain intermediate coloured substances (Caramelane and Caramelene of Gélis) to diffuse out with considerable facility, while the compound containing the largest proportion of carbon remains behind. The latter substance, as obtained by me, possessed five times the colouring power of the original crude caramel, weight for weight. This highest soluble member of the caramel series may also be obtained, more quickly, by precipitation from its aqueous solution by means of alcohol. But I found it necessary to repeat the precipitation four times, or till the mass thrown down, from being plastic at first became pulverulent. A solution containing 10 per cent. of the caramel so purified was gummy; and on standing, it formed a tremulous jelly entirely soluble in hot or cold water. Evaporated *in vacuo*, the solution dries up into a black shining mass, which is tough and elastic, while it still possesses a certain proportion of water, like gum containing some water. Once thoroughly dried at a low temperature, this soluble caramel may be heated, afterwards, to 120° and retain complete solubility. But if a solution of the same

* Ann. Ch. Phys. [3], lii, 352.

caramel be directly evaporated to dryness by the heat of a water-bath, the whole matter is rendered insoluble in hot or cold water. The soluble and insoluble caramel have the same composition, and appear to illustrate the usual double form of colloids. The proportion of carbon in the fluid caramel was found as high as 54·59 per cent., which comes nearer to $C_{24}\,H_{13}\,O_{13}$ (requiring C 55·17) than any other formula in which the oxygen and hydrogen are assumed to be present in the proportion of water. In the analysis by Gélis of his caramelin, the proportion of carbon did not exceed 51·33 per cent., which does not apply to the present substance.

Fluid caramel is wholely tasteless, and appears to be neutral. It exhibits the same excessive sensibility to crystalloidal reagents which is witnessed in fluid silicic acid and alumina. The solution is precipitated or pectized by mere traces of any mineral acid, by alkaline sulphates, chloride of sodium, by most other salts, and by alcohol. The caramel then forms a brownish black pulverulent substance, insoluble in hot or cold water. The presence of sugar and of the intermediate brown substances protects fluid caramel in a remarkable way from the action of crystalloids, and accounts for the preceding properties not being observed in crude caramel. This colloid appears also to be precipitated by certain substances of its own class, such as peroxide of iron.

Pectous caramel may readily have its solubility restored. Placed in dilute potash, the caramel swells and appears gelatinous, and is dissolved on the application of heat. When this solution is dialysed, the potash is quickly reduced to the proportion of about 9 per cent., which forms a neutral compound. If an excess of acetic acid be now added, the whole potash is soon diffused away, and pure soluble caramel remains on the dialyser. Even carbonic acid will carry away the potash.

The extremely low diffusibility which has been assigned to caramel in former Tables, belongs to that substance as last described; the brown intermediate substances which accompany it in crude caramel are considerably more diffusive, although they again are much less diffusive than any variety of crystallizable or uncrystallizable sugar. When the molasses of the cane-sugar are diffused, much the greater portion of the colouring matters remains in the dialyser.

With the parchment-paper septum the fluid caramel appeared even less dialysable than gum, the diffusate in twenty-four hours from a 2 per cent. solution of the former being ·009 gramme only,

while that of the latter was ·013. Caramel may be stated, approximately, to be 600 times less dialysable than chloride of sodium, and 200 times less so than sugar. Hence liquids coloured with caramel, such as porter and coffee, may be dialysed for a day with the passage of very little colouring matter.

Before leaving caramel, the analogy may be referred to which the insoluble form of that substance presents to *coal*. Caramelization appears the first step in that direction,—the beginning of a colloidal transformation to be consummated in the slow lapse of geological ages.

Albumin.—The purification of albumin is effected with much advantage upon the dialyser. The solution of egg-albumin is mixed freely with acetic acid and then dialysed. The earthy and alkaline salts are speedily got rid of, and in three or four days the albumin burns without leaving a trace of ash. Although the acetic acid used in the process appears to diffuse off entirely, albumin prepared in the manner described has a faint acid reaction. It also coagulates milk when mixed with the latter and heated. Albumin so prepared retains its constituent sulphur.

The passage through parchment-paper of pure albumin prepared by the unobjectionable process of M. Wurtz is so slow, that several days are required to produce a sensible result. Thus the diffusate from a solution of 2 grammes of albumin in 50 grammes of water was 0·052 gramme in eleven days, which gives 0·005 gramme in a single day. Albumin, then, appears to be about $2\frac{1}{2}$ times less dialysable than gum, and 1,000 times less so than chloride of sodium.

Even combination with an alkali does not appear to enable albumin to pass through the colloid septum. To half a gramme of pure albuminic acid dissolved in 50 grammes of water, ·05 gramme of hydrate of soda was added (one-tenth of the weight of the albumin), and the liquid was placed upon parchment-paper. No albumin could be discovered in the diffusate of several days, but it gave ·069 gramme of carbonate of soda, equivalent to ·053 gramme of hydrate of soda; that is the whole soda originally added to the albumin. The separation of the soda from the albumin may possibly have been aided by the presence of carbonic acid in the water, but certainly the entire separation of the alkali from albumin by diffusion through a colloidal film is a remarkable fact. Hydrate of potash was found to diffuse away from albumin in the same manner.

A solution of *Emulsin* is precipitated by albuminic and gummic acids, but not by unpurified albumin or gum-arabic. The precipitates are white and opaque, pulverulent, and not gelatinous. They are soluble in acetic acid.

A thin stratum of pure albumin coagulated by heat appears to intercept completely the passage of liquid albumin of the egg. Forty grammes of undiluted egg-albumin, representing 5·6 grammes of dry albumin, were placed on a dialyser of the small size, composed of two sheets of calico well-impregnated with albumin and coagulated by heat of steam, as in the albuminized osmometer*. After twelve days the volume of liquid within the instrument had increased to 117 grammes by osmose, while a diffusate had passed through the dialyser of 0·243 gramme, or 4·34 per cent. of the original dry albumin. This diffusate consisted of salts chiefly, with some organic matter, but no portion of the latter was coagulable by heat.

Neither gelatinous starch, animal gelatin dissolved in water, nor extract of flesh, appears to be capable of diffusing through a colloid septum in a sensible degree, although salts and other crystallizable substances, which are mixed with the former, diffuse through the septum readily, and may thus be separated from the former substances.

6. *Separation of Arsenious Acid from Colloidal Liquids.*

Dialysis may be advantageously applied to the separation of arsenious acid and metallic salts from organic solutions in medico-legal inquiries. The process has the advantage of introducing no metallic substance or chemical reagent of any kind into the organic fluid. The arrangement for operating is also of the simplest nature.

The organic fluid is placed, to the depth of half an inch, on a dialyser formed of a hoop of gutta percha 10 or 12 inches in diameter, covered with parchment-paper (fig. 1, page 220). The dialyser is then floated in a basin containing a volume of water about four times greater than the volume of organic fluid in the dialyser. The water of the basin is generally found to remain colourless after the lapse of twenty-four hours, and after being concentrated by evaporation, it admits of the application of the proper reagents to precipitate and remove a metal from solution.

* Philosophical Transactions, 1854, p. 189.

One-half to three-fourths of the crystalloidal and diffusible constituents of the organic fluid will generally be found in the water of the basin.

In the few illustrative experiments which follow, the 4-inch bulb dialyser, having an area of 16 square inches, or about $\frac{1}{100}$dth part of a square meter, was generally made use of (fig. 3, page 239). The volume of liquid placed in the bulb was 50 cubic centimeters, and accordingly covered the dialyser to a depth of 5 millimeters, or about 0.2 inch. The outer volume of water (in the jar) was not less than 1 litre, or twenty times the volume of the solution on the dialyser.

1. A solution of arsenious acid, in pure water, was first placed on the dialyser, the water containing 0·5 per cent. of arsenious acid, or 0·25 gramme of that substance, for twenty-four hours. The dialyser being then removed, the outer fluid was concentrated by heat, and then precipitated by sulphuretted hydrogen. It gave 0·300 gramme of tersulphide of arsenic, equivalent to 0·241 gramme of arsenious acid. It appears, then, that about 95 per cent. of the arsenious acid had diffused from the dialyser into the water-jar in twenty-four hours.

2. Water, with one-fourth of its volume of fluid egg-albumin and 0·25 gramme, or 0·5 per cent. of arsenious acid, was now placed on the dialyser as before. The diffusate gave, with sulphuretted hydrogen, after being acidulated with hydrochloric acid, 0·267 gramme of tersulphide of arsenic, equivalent to 0·214 gramme of arsenious acid.

3. The water contained 10 per cent. of gum-arabic and 1 per cent. arsenious acid, the latter amounting to 0·5 gramme. From the diffusate was derived 0·505 gramme of tersulphide of arsenic, equivalent to 0.406 gramme of arsenious acid. The dialyser still gave out arsenious acid when immersed for a second day in water. The outer fluid contained no gum.

It may be added that a similar 1 per cent. solution of arsenious acid, without the gum, gave a diffusate of 0·45 gramme arsenious acid in the same time, that is, nine-tenths of the whole acid.

4. A solution in hot water of 1 per cent. isinglass and 0·5 per cent. of arsenious acid (0·25 gramme), formed a jelly upon the dialyser on cooling. The diffusate from the jelly gave 0·260 tersulphide of arsenic, equivalent to 0·209 arsenious acid, with no gelatine. The escape of the arsenious acid appears then to have been slightly retarded by the fixing of the gelatinous solution.

This is probably due to the arrest of mechanical movement within the gelatinous stratum, and not to any sensible impediment offered by the jelly to diffusion.

In another experiment, similar to the last, but continued for four days instead of twenty-four hours, the tersulphide of arsenic weighed 0·320 gramme, equivalent to 0·257 arsenious acid.

5. A quantity of white of egg, amounting to 50 grammes, to which 0·01 gramme of arsenious acid in solution had been added, was coagulated by heat. The solid mass was then cut up into small pieces and placed on the dialyser, mixed with 50 grammes of water; after the usual period of twenty-four hours, the diffusate gave 0·01 gramme of tersulphide of arsenic, equivalent to 0·008 gramme arsenious acid. Here, of the mass upon the dialyser, the arsenious acid formed only $\frac{1}{10,000}$dth part, yet four-fifths of it were recovered.

6. One hundred grammes of milk, charged with $\frac{1}{10,000}$dth part of arsenious acid (0·01 gramme), and forming a stratum on the dialyser of 10 millimeters, gave a diffusate which yielded 0·010 tersulphide of arsenic, equivalent to 0·008 gramme of arsenious acid. The outer liquid was colourless, and gave no indication of casein, but it contained of course the salts and the sugar of the milk.

7. The same experiment was repeated with sized writing-paper, as the septum, applied to the same bulb. The result was a slight increase in the quantity of arsenious acid recovered.

It appears, then, that arsenious acid separates on the dialyser from gum, from gelatine, albumin, fluid or coagulated, and from casein, and is obtained in a solution fit for the application of reagents.

8. Half a litre of dark-coloured porter, with 0·05 gramme of arsenious acid added ($\frac{1}{10,000}$dth part of arsenious acid) was placed on a hoop dialyser, 8 inches in diameter, and the whole floated in an earthenware basin containing two or three litres of water. After twenty-four hours, the latter fluid had acquired a slight tinge of yellow. It yielded, when concentrated and precipitated by sulphuretted hydrogen, upwards of one-half of the original arsenious acid in a fit state for examination.

9. In a similar experiment on 200 grammes of defibrinated blood charged with $\frac{1}{4000}$dth part of arsenious acid (0·05 gramme), and placed in a similar dialyser to the last for twenty-four hours,

the diffusate of arsenious acid was recovered with the same facility, and appeared to be equally considerable.

10. Animal intestines, charged with the usual minute proportion of arsenious acid, were cut into small pieces and digested in water, about 32° C., for twenty-four hours. The whole was then thrown upon a dialyser for an equal time. Arsenious acid diffused out so free from colloidal matter that the action of reagents was not interfered with. A high temperature in digesting the intestines is quite unnecessary, and appeared indeed to increase the difficulty of diffusing out the arsenious acid afterwards.

The *tartrate of potash and antimony*, mixed in a small proportion of $\frac{1}{10,000}$dth, with defibrinated blood and with milk, was separated by dialysis quite as effectually as arsenious acid above.

Strychnine also was separated from organic fluids in the same manner, a small addition of hydrochloric acid being first made to the fluid on the dialyser.

Dialysis then appears of general application in the preparation of a liquid for examination by chemical tests, whether the poison looked for be mineral or organic. All soluble poisonous substances, whatever their origin, appear to be crystalloids, and accordingly pass through collodial septa.

7. *Colloidal Condition of Matter.*

I may be allowed to advert again to the radical distinction assumed in this paper to exist between colloids and crystalloids in their intimate molecular constitution. Every physical and chemical property is characteristically modified in each class. They appear like different worlds of matter, and give occasion to a corresponding division of chemical science. The distinction between these kinds of matter is that subsisting between the material of a mineral and the material of an organized mass.

The colloidal character is not obliterated by liquefaction, and is therefore more than a modification of the physical condition of solid. Some colloids are soluble in water, as gelatin and gum-arabic; some are insoluble, like gum-tragacanth. Some colloids, again, form solid compounds with water, as gelatin and gum-tragacanth, while others, like tannin, do not. In such points the colloids exhibit as great a diversity of property as the crystalloids. A certain parallelism is maintained between the two classes, notwithstanding their differences.

The phenomena of the solution of a salt or crystalloid probably all appear in the solution of a colloid, but greatly reduced in degree. The process becomes slow, time indeed appearing essential to all colloidal changes. The change of temperature, usually occurring in the act of solution, becomes barely perceptible. The liquid is always sensibly gummy or viscous when concentrated. The colloid, although often dissolved in a large proportion by its solvent, is held in solution by a singularly feeble force. Hence colloids are generally displaced and precipitated by the addition to their solution of any substance from the other class. Of all the properties of liquid colloids, their slow diffusion in water, and their arrest by colloidal septa, are the most serviceable in distinguishing them from crystalloids. Colloids have feeble chemical reactions, but they exhibit at the same time a very general sensibility to liquid reagents, as has already been explained.

While soluble crystalloids are always highly sapid, soluble colloids are singularly insipid. It may be questioned whether a colloid, when tasted, ever reaches the sentient extremities of the nerves of the palate, as the latter are probably protected by a colloidal membrane, impermeable to soluble substances of the same physical constitution.

It has been observed that vegetable gum is not digested in the stomach. The coats of that organ dialyse the soluble food, absorbing crystalloids and rejecting all colloids. This action appears to be aided by the thick coating of mucus which usually lines the stomach.

The secretion of free hydrochloric acid during digestion—at times most abundant—appears to depend upon processes of which no distinct conception has been formed. But certain colloidal decompositions are equally inexplicable upon ordinary chemical views. To facilitate the separation of hydrochloric acid from the perchloride of iron, for instance, that salt is first rendered basic by the addition of peroxide of iron. The comparatively stable perchloride of iron is transformed, by such treatment, into a feebly-constituted colloidal hydrochlorate. The latter compound breaks up under the purely physical agency of diffusion, and divides on the dialyser into colloidal peroxide of iron and free hydrochloric acid. The super-induction of the colloidal condition may possibly form a stage in many analogous organic decompositions.

A tendency to spontaneous change, which is observed occasionally in crystalloids, appears to be general in the other class. The

fluid colloid becomes pectous and insoluble by contact with certain other substances, without combining with these substances, and often under the influence of time alone. The pectizing substance appears to hasten merely an impending change. Even while fluid a colloid may alter sensibly, from colourless becoming opalescent; and while pectous the degree of hydration may become reduced from internal change. The gradual progress of alteration in the colloid effected by the agency of time, is an investigation yet to be entered upon.

The equivalent of a colloid appears to be always high, although the ratio between the elements of the substance may be simple. Gummic acid, for instance, may be represented by $C_{12}H_{11}O_{11}$, but judging from the small proportions of lime and potash which suffice to neutralize this acid, the true numbers of its formula must be several times greater. It is difficult to avoid associating the inertness of colloids with their high equivalents, particularly where the high number appears to be attained by the repetition of a smaller number. The inquiry suggests itself whether the colloid molecule may not be constituted by the grouping together of a number of smaller crystalloid molecules, and whether the basis of colloidality may not really be this composite character of the molecule.

With silicic acid, which can exist in combination both as a crystalloid and colloid, we have two series of compounds, silicates and cosilicates, the acid of the latter appearing to have an equivalent much greater (thirty-six times greater in one salt) than the acid of the former. The apparently small proportion of acid in a variety of metallic salts, such as certain red salts of iron, is accounted for by the high colloidal equivalent of their bases. The effect of such an insoluble colloid as prussian blue in carrying down small proportions of the precipitating salts, may admit of a similar explanation.

Gelatin appears to hold an important place as a colloidal base. This base unites with colloidal acids, giving a class of stable compounds, of which tanno-gelatin only appears to be hitherto known. Gelatin is precipitated entirely by a solution of metaphosphoric acid added drop by drop, 100 parts of gelatin uniting with 3·6 parts of the acid. The compound formed is a semitransparent, soft, elastic, and stringy solid mass, presenting a startling resemblance to animal fibrin. It will be an interesting inquiry whether metaphosphoric acid is a colloid, and enters into the com-

pound described in that character, or is a crystalloid, as the small proportion and low equivalent of the acid would suggest. Gelatin is also precipitated by carbolic acid.

The hardness of the crystalloid, with its crystalline planes and angles, is replaced in the colloid by a degree of softness, with a more or less rounded outline. The water of crystallization is represented by the water of gelatination. The water in gelatinous hydrates is aptly described by M. Chevreul as retained by "capillary affinity," that is, by an attraction partaking both of the physical and chemical character. While it is here admitted that chemical affinity of the lowest degree may shade into capillary attraction, it is believed that the character of gelatinous hydration is as truly chemical as that of crystalline hydration. Combination of a colloid with water is feeble, it is true, but so is combination in general with the colloid. Notwithstanding this, anhydrous colloids can decompose certain crystalloid hydrates. The water in alcohol of greater strength than corresponds with the density 0·926, which represents the definite hydrate $C_4H_6O_2+6\,HO$, is certainly in a state of chemical union. But alcohol so high as 0·906, contained in a close vessel, is concentrated in a notable degree by contact with dry mucus, gelatin, and gum, and sensibly even by dry parchment-paper. Dilute alcohol divided from the air of the atmosphere by a dry septum of mucus, gelatin, or gum, is also concentrated by evaporation, as it is in the well-known bladder experiment of Sömmering. The selective power is here apparent of the colloid for water, that fluid being separated from alcohol, and travelling through the colloidal septum by combination with successive molecules of the latter, till the outer surface is reached and evaporation takes place. The penetration in this manner of a colloid by a foreign substance may be taken as an illustration of the phenomena of cementation. Iron and other substances which soften under heat, may be supposed to assume at the same time a colloidal constitution. So it may be supposed does silica when fused into a glass by heat; and every other vitreous substance.

Gelatinous hydrates always exhibit a certain tendency to aggregation, as is seen in the jelly of hydrated silicic acid and of alumina. With some the jelly is also adhesive, as in glue and mucus. But unless they be soluble in water, gelatinous hydrates, when once formed, are not always adhesive. Separated masses do not reunite when brought into contact. This want of adhesiveness is

very remarkable in the gelose of Payen, which resembles gelatin so closely in other respects. Layers of a gelose solution, allowed to cool and gelatinize in succession in a diffusion-jar (p. 199), do not adhere together.

Ice itself presents colloidal characters at or near its melting-point, paradoxical although the statement may appear. When ice is formed at temperatures a few degrees under 0°C., it has a well-marked crystalline structure, as is seen in water frozen from a state of vapour, in the form of flakes of snow and hoar-frost, or in water frozen from dilute sulphuric acid, as observed by Mr. Faraday. But ice formed in contact with water at 0°, is a plain homogeneous mass with a vitreous fracture, exhibiting no facets or angles. This must appear singular when it is considered how favourable to crystallization are the circumstances in which a sheet of ice is slowly produced in the freezing of a lake or river. The continued extrication of latent heat by ice as it is cooled a few degrees below 0°C., observed by M. Person, appears also to indicate a molecular change subsequent to the first freezing. Further, ice, although exhibiting none of the viscous softness of pitch, has the elasticity and tendency to rend seen in colloids. In the properties last mentioned, ice presents a distant analogy to gum incompletely dried, to glue, or any other firm jelly. Ice further appears to be of the class of adhesive colloids. The redintegration (regelation of Faraday) of masses of melting ice, when placed in contact, has much of a colloid character. A colloidal view of the properties of ice indicated in the glacier movement will readily develope itself.

A similar extreme departure from its normal condition appears to be presented by a colloid holding so high a place in its class as albumin. In the so-called blood-crystals of Funke, a soft and gelatinous albuminoid body is seen to assume a crystalline contour. Can any facts more strikingly illustrate the maxim that in nature there are no abrupt transitions, and that distinctions of class are never absolute?

8. *Osmose.*

Little has been said in the present paper respecting osmose, a subject closely connected with colloidal septa. It now appears to me that the water movement in osmose is an affair of hydration and of dehydration in the substance of the membrane or other colloid septum, and that the diffusion of the saline solution placed within the osmometer has little or nothing to do with the osmotic

result, otherwise than as it affects the state of hydration of the septum.

Osmose is generally considerable, through membranous and other highly hydrated septa, with the solution of any colloid (gum, for instance) contained in the osmometer. Yet the diffusion outwards of the colloid is always minute, and may sometimes amount to nothing. Indeed, an insoluble colloid, such as gum-tragacanth, placed in powder within the osmometer, was found to indicate the rapid entrance of water, to convert the gum into a bulky gelatinous hydrate. Here no outward or double movement is possible.

The degree of hydration of any gelatinous body is much affected by the liquid medium in which it is placed. This is very obvious in fibrin and animal membrane. Placed in pure water, such colloids are hydrated to a higher degree than they are in neutral saline solutions. Hence the equilibrium of hydration is different on the two sides of the membrane of an osmometer. The outer surface of the membrane being in contact with pure water tends to hydrate itself in a higher degree than the inner surface does, the latter surface being supposed to be in contact with a saline solution. When the full hydration of the outer surface extends through the thickness of the membrane and reaches the inner surface, it there receives a check. The degree of hydration is lowered, and water must be given up by the inner layer of the membrane, and it forms the osmose. The contact of the saline fluid is thus attended by a continuous catalysis of the gelatinous hydrate, by which it is resolved into a lower gelatinous hydrate and free water. The inner surface of the membrane of the osmometer contracts by contact with the saline solution, while the outer surface dilates by contact with pure water. Far from promoting this separation of water, the diffusion of the salt throughout the substance of the membrane appears to impede osmose, by equalizing the condition as to saline matter of the membrane through its whole thickness. The advantage which colloidal solutions have in inducing osmose, appears to depend in part upon the low diffusibility of such solutions, and their want of power to penetrate the colloidal septum.

The substances fibrin, albumin, and animal membrane swell greatly when immersed in water containing minute proportions of acid or of alkali, as is well known. On the other hand, when the proportion of acid or alkali is carried beyond a point peculiar to each substance, contraction of the colloid takes place. Such colloids as

have been named acquire the power of combining with an increased proportion of water, and of forming superior gelatinous hydrates, in consequence of contact with dilute acid or alkaline reagents. Even parchment-paper is more elongated in an alkaline solution than in pure water. When so hydrated and dilated, the colloids present an extreme osmotic sensibility. Used as septa, they appear to assume or resign their water of gelatination under influences apparently the most feeble. It is not attempted to explain this varying hydration of colloids with the osmotic effects thence arising. Such phenomena belong to colloidal chemistry, where the prevailing changes in composition appear to be of the kind vaguely described as catalytic. To the future investigation of catalytic affinity, therefore, must we look for the further elucidation of osmose.

XXXVI.—*On the Composition of the Aqueous Acids of Constant Boiling Point.—Second Communication.*

By Henry Enfield Roscoe.

In a paper published in volume XIII of the *Quarterly Journal of the Chemical Society*, I showed that the acid liquids of constant composition obtained by distilling, under the ordinary atmospheric pressure, aqueous acids of very different degrees of strength, cannot be regarded as definite chemical combinations of acid and water, because, in the first place, their constituents are not, with one fortuitous exception, contained in simple atomic proportions; and, secondly, because these acid liquids undergo a gradual alteration in composition when exposed to a gradual alteration of physical condition, such as change of the temperature of ebullition.

I proved, on distilling aqueous sulphuric, nitric, hydrochloric, hydrobromic, hydriodic, and hydrofluoric acids of various strengths at different temperatures, that for every temperature each acid attains a particular constant composition and reaches a fixed boiling point; and I concluded that in these cases the resulting composition is determined rather by physical than by chemical attractions. I have since, likewise shown* that aqueous perchloric acid comports itself on distillation in an analogous manner. I have now to add

* "On Perchloric Acid and its hydrates."—Proceedings of the Royal Society, vol. xi, p. 493.

to these results a description of the phenomena attending the distillation of aqueous formic and acetic acids.

1. *Formic Acid.*

According to Liebig,* an aqueous formic acid containing one atom of water (H_2O) to two atoms of real acid (CH_2O_2), and boiling at the fixed temperature of 106°C., is obtained by distilling 18 parts of formate of lead with 6 parts of oil of vitriol and 1 part of water, the real acid, according to the same chemist, boiling at 98°·5 C. In order to obtain further evidence respecting the composition of this aqueous acid of constant boiling point, pure glacial formic acid was prepared by decomposing formate of lead with dry sulphuretted hydrogen and rectification over an excess of the dry lead-salt. The boiling point of the acid thus obtained was found by Kopp's method to be 101°·1 C. under a pressure of 758 mm. of mercury†. The first portions of the distillate were solidified, and after one-third of the glacial acid had been removed by melting, the residue was analysed with standard soda, and found to contain 100·2 per cent. of pure formic acid. Another portion of the same acid was distilled to one-fifth of its volume, and the residue analysed, first by soda and secondly by neutralization with pure carbonate of barium, the barium in solution being estimated as sulphate. According to the soda analysis, the substance contained 100·0 per cent. of formic acid; according to the barium determination, it contained 99·72 per cent.

The pure acid was mixed with water in different proportions, the liquids distilled under the ordinary atmospheric pressure to a known fraction of their original bulk, and the composition of the residue determined. From a series of experiments thus made, it appears that a liquid containing 77·5 parts of acid to 22·5 parts of water undergoes no change by distillation under a pressure of 760 mm. of mercury, boiling at the fixed temperature of 107°·1 C.; and that all mixtures containing more acid or more water than this quantity, when distilled under the above conditions, ultimately attain this same fixed boiling point and constant composition. The following table contains the results of the experiments:— Column I. gives the volume of liquid employed; column II. the percentage of real acid contained in this liquid; column III.

* Handwörterbuch der Chemie, 1842. Article "Ameisensäure."

† It is remarkable that Kopp gives the boiling point of pure formic acid at 105°·3 C under a pressure of 760 mm.

the volume of liquid remaining after distillation; column IV. the percentage of real acid contained in the residual liquid.

I.—Distillation of Aqueous Formic acid under the ordinary atmospheric pressure.

No.	I.	II.	III.	IV.	No.	I.	II.	III.	IV.
	cbc.		cbc.			cbc.		cbc.	
1	1000	6·7	250	12·8	10	30	77·7	5	77·5
2	250	12·8	60	28·4	11	30	78·2	5	77·6
3	60	28·4	15	43·4	12	30	78·5	5	77·6
4	15	43·4	5	60·7	13	30	78·6	5	78·3
5	30	74·1	5	75·8	14	30	80·4	5	79·2
6	30	77·0	5	77·3	15	30	80·9	5	78·9
7	30	77·1	5	77·5	16	30	87·6	5	80·6
8	30	77·3	5	77·4	17	30	92·5	5	85·9
9	30	77·3	5	77·4	18	30	97·4	5	90·4

Distilled under a higher pressure, this aqueous acid undergoes a change of composition. Under a pressure of 1·83 metre of mercury, the residual liquid attains a constant composition of 83·2 per cent. of real acid, and boils unchanged at 134°·6 C. The numbers have the same signification as in the preceding table.

II.—Distillation of Aqueous Formic acid under pressures greater than that of the atmosphere. (1) Pressure = 1·83 metre of mercury.

No.	I.	II.	III.	IV.	No.	I.	II.	III.	IV.
	cbc.		cbc.			cbc.		cbc.	
1	30	77·5	5	83·2	5	30	83·0	5	83·2
2	30	81·2	5	81·6	6	30	83·1	5	83·2
3	30	81·7	5	82·3	7	30	83·8	5	83·3
4	30	82·4	5	82·7					

(2) Pressure = 1·35 metre of mercury.

No.	I.	II.	III.	IV.
1	30 cbc.	77·8	5 cbc.	78·4
2	30 —	79·2	5 —	79·5
3	30 —	79·5	5 —	80·0
4	30 —	80·3	5 —	79·9

The liquid containing 80 per cent. of real acid boiled under a pressure of 1·35 metre of mercury at the fixed temperature of 124°·1 C.

In order to determine the relation between the quantities of acid and water existing in the liquid which vaporizes at the ordinary atmospheric temperature without undergoing change of composition, dry air was passed through aqueous formic acid of various degrees of strength until the residual liquid did not alter its composition. The results of the experiment are found in the following table, in which column I. gives the percentage of real acid contained in the liquid before passage of dry air through it; column II. the time during which the air passed; column III. the temperature of the liquid during the experiment; column IV. the fraction of the original volume to which the liquid was ultimately reduced; and column V. the percentage of real acid contained in the residual liquid.

III.—Passage of dry air through Aqueous Formic acid at the ordinary atmospheric temperature.

No.	I.	II.	III.	IV.	V.
1	77·3	24 hours	14°—15°C	$\frac{1}{2}$	77·1
2	77·1	8 —	15°C	$\frac{1}{2}$	68·4
3	68·4	24 —	12°—16°C	$\frac{1}{2}$	61·2
4	61·0	8 —	12°—15°C	$\frac{3}{4}$	60·3
5	60·3	16 —	14°—15°C	$\frac{1}{2}$	60·4
6	58·9	24 —	14°—15°C	$\frac{1}{2}$	59·6
7	59·6	16 —	12°C	$\frac{1}{4}$	59·3

From the above experiments it is clear that formic acid possesses no hydrate of simple atomic constitution having a constant boiling point; but that any number of mixtures of formic acid and water can be made, each one of which, distilled under a given pressure, will undergo no change in composition, and, therefore, must boil at a fixed point. In this respect, then, the behaviour of formic acid is exactly similar to that of the aqueous acids previously examined.

2. *Acetic Acid.*

It is well known that weak acetic acid gives on distillation a more watery distillate and a stronger residual acid. It is likewise

stated in most Handbooks* that the aqueous acid containing 77 per cent. of real acetic acid ($C_2H_4O_2$), having the maximum density, and containing one atom of acid to one of water (H_2O), can be distilled without undergoing change, and boils at the fixed temperature of 104°C. The following experiments show that this latter statement is incorrect, and that no aqueous acetic acid exists which boils unchanged at a fixed temperature. It will be seen that acetic acid and water, when mixed in any proportions whatever, can be separated by distillation, the residue ultimately consisting of glacial acid; so that, in this respect, acetic acid differs from all the aqueous acids previously examined.

The analysis of the aqueous acetic acids was made with standard soda: 1006 equivalents of thrice recrystallised glacial acid being required to give the neutral litmus reaction with 1000 equivalents of soda.

I.—Distillation of aqueous acetic acid under the ordinary atmospheric pressure.

(1) A litre of aqueous acid containing 32·5 per cent. of real acid was distilled, the successive distillates and the residue being analysed. Column I. gives the volume of the distillate; column II. the percentage of real acid which each distillate contained:

No.	I.	II.	No.	I.	II.
1	50 cbc.	21·9	8	100 cbc.	28·8
2	100 —	23·6	9	100 —	33·7
3	50 —	23·2	10	50 —	37·1
4	75 —	23·2	11	50 —	40·1
5	100 —	25·2	12	50 —	45·1
6	100 —	26·8	13	50 —	65·8
7	100 —	28·7			

The residue of 25 cbc. contained 80·3 per cent. of real acid.

(2) 180 cbc. of a liquid containing 80·7 per cent. of real acid was distilled; three successive distillates contained 73·1, 81·0, and 89·3 per cent. of acid respectively; the residue of 20 cbc. contained 96·1 per cent of acid.

* See Handwörterbuch der Chemie, article "Essigsaüre;" also Kekulé "Lehrbuch der Organischen Chemie," p. 563.

(3) 270 cbc. of a liquid containing 81·4 per cent. of real acid was distilled; five successive distillates contained 71·8, 74·4, 77·4, 81·6, and 85·2 per cent. of real acid respectively; the residue of 20 cbc. contained 97·9 per cent. of acid, and solidified on cooling.

(4) 50 cbc. of a liquid containing 77·5 per cent. of acid began to boil at 103°C. (Barom. = 760 m.m.); on distilling to $\frac{1}{6}$ of the original volume the boiling point rose to 113°C., and the residue contained 95·6 per cent. of acid.

(5) 50 cbc. of a liquid containing 79·0 per cent. of acid began to boil at 103°·3 C.; on distilling to $\frac{1}{6}$ the temperature rose to 112°C., and the residue contained 96·3 per cent. of acid.

(6) 50 cbc. of a liquid containing 80·0 per cent. of acid began to boil at 104°C.; on distilling to $\frac{1}{6}$ the temperature rose to 114°C., and the residue contained 96·8 per cent. of acid.

(7) 250 cbc. of a liquid containing 88·2 per cent. of acid on distillation to 15 cbc. left a residue which solidified on cooling, and contained 98·6 per cent. of real acid.

(8) 50 cbc. of a liquid containing 96·7 per cent. of acid, on distillation to 15 cbc. left a residue which solidified on cooling, and contained 98·8 per cent. of real acid.

(9) 50 cbc. of a liquid containing 91·7 per cent. of acid, on distillation to 15 cbc. left a residue which solidified on cooling, and contained 99·6 per cent. of real acid.

From these determinations it is seen, that aqueous acetic acid, distilled under the ordinary atmospheric pressure, splits up into water and glacial acid. The same result was obtained by distilling under pressures both greater and less than that of the atmosphere, as the following numbers show:—

II.—Distillation of aqueous acetic acid under pressures greater than that of the atmosphere:

Pressure = 1·340 metre of mercury.

(1) 60 cbc. of a liquid containing 81·4 per cent. of acid, on distillation to 15 cbc. left a residue containing 95·3 per cent. of acid.

(2) 60 cbc. of a liquid containing 90·7 per cent. of acid, on distillation to 10 cbc. yielded a residue which solidified on cooling, and contained 99·3 per cent. of acid.

III.—Distillation of aqueous acetic acid under pressure less than that of the atmosphere.

Pressure = 40 mm. of mercury.

(1) 50 cbc. of liquid containing 81·4 per cent. of acid, on distillation yielded a residue of 5 cbc. containing 92·5 per cent. of real acid.

(2) 50 cbc. of liquid, containing 89·7 per cent. of acid, on distillation gave a residue of 5 cbc. containing 95·1 per cent. of acid.

(3) 50 cbc. of liquid, containing 95·8 per cent. of acid, on distillation gave a residue of 5 cbc. which solidified on cooling, and contained 99·4 per cent. of acid.

The following determinations of the specific gravity of different aqueous acetic acids near the relation $C_2H_4O_2$ to H_2O, closely agree with Van Toorn's results*, and show that the aqueous acids containing from 76·5 to 80·0 per cent. of real acid possess the same specific gravity, so that no point of maximum density exactly corresponding to the compound of one of water to one of acid exists.

Per cent. of real acid.	Specific gravity at 15°·5 C.
76·5	1·0751 1·0753
77·5	1·0754 1·0754
79·0	1·0754
80	1·0754
98·5	1·0597
100·0	1·0563 1·0565

I beg to thank Mr. Schorlemmer for the aid which he gave me in carrying out the above experiments.

* J. pr. Chem., 6, 171.

XXXVII.—*On Sombrerite.*

By Dr. T. L. Phipson, F.C.S.,
Member of the Chemical Society of Paris, &c., &c.

This mineral forms a large portion of some small islands in the West Indies, especially of Sombrero Island (N. lat. 18° 35′, W. long. 63° 28′), about 60 miles from St. Thomas. Its composition and properties prove it to be a new species, to which I have given the name sombrerite. It is remarkable for the large proportion of phosphoric acid it contains.

Sombrerite presents itself in nature as a white, yellowish white, or reddish coloured rock, having a straight fracture and, in some portions, a peculiar horny aspect; its appearance is, in general, compact, though, in reality, the rock is very porous. It shows no signs of crystallisation whatever, but appears like an amorphous, gelatinous phosphate that has been submitted to a high temperature. It is thought to be of comparatively recent geological origin, as it encloses fossil bones (of mammalia?) and several kinds of shells. In a mineralogical point of view, sombrerite is a compound of phosphate of lime with phosphate of alumina; in some specimens a portion of the alumina is replaced by a corresponding proportion of sesquioxide of iron; in others, where little or no iron is present, the mineral adheres to the tongue like other aluminiferous minerals. Sombrerite is not phosphorescent by heat like apatite; before the blowpipe, when moistened with sulphuric acid, it colours the flame pale green. It contains no fluoride or chloride of calcium.

The specific gravity of sombrerite is 2·52. A well-chosen specimen has given me the following composition:—

		Atomic ratio.	
Water	9·00	1·00	20
Phosphate of lime $\dot{Ca}^3\ddot{P}$ ..	65·00	0·41	8
Phosphate of alumina $\dot{Al}^2\ddot{P}^3$ ..	17·00	0·05	1
Carbonate of lime	5·00		
Chloride of sodium	1·44		
Sulphate of lime	1·36		
Silica	1·00		
Crenate of ammonia, &c. ..	0·20		
	100·00		

The formula of sombrerite is therefore $8\dot{Ca}^3\ddot{P} + \dot{Al}^2\ddot{P}^3 + 20\dot{H}$

Persons who have seen this rock think that it owes its origin to guano, some looking upon it as "fossil guano," and others as "guano modified by volcanic action." In order to bring forward, if possible, some proof of these theories, I took a large quantity of the mineral and sought carefully for uric acid. Though the experiment was repeated several times, I have not been able to find the least trace of that compound, but only a very small quantity of *crenate of ammonia*, which I have frequently met with in many other minerals, notably in iron ores of various ages. At the same time it is possible that sombrerite may have derived its origin from ancient deposits of guano, modified by time and geological phenomena, as we see large beds of limestone and sandstone almost completely formed by the *débris* of organised beings. However that may be, I look upon this rock as having found its way to the surface at a high temperature, in contact with water or steam, and under great pressure. This would account for its peculiar appearance.

As regards the uses of sombrerite, I believe it has been employed already for the preparation of phosphorus, phosphoric acid, &c. But for agricultural purposes, though doubtless valuable, it presents a drawback to the manufacturer of "super-phosphate of lime." In producing the latter, sombrerite gives rise to a certain quantity of sulphate of alumina, and this salt being deliquescent, attracts and retains so much moisture that the product can be dried only with great difficulty.

Sombrerite has, however, the advantage of being easily reduced to powder, and could, in that state, be advantageously mixed with certain soils.

XXXVIII.—*Note on the Sulphur-compound formed by the action of Sulphuretted Hydrogen on Formate of Lead at a high temperature.*

By W. J. Hurst,

Student in the Laboratory of Owens College, Manchester.

In the year 1856, Limpricht* published an account of some analyses of a crystalline body, obtained together with formic acid

* Ann. Ch. Pharm., xcvii. 361.

by acting upon formate of lead heated to 200°—300°C with a current of sulphuretted hydrogen. As the result of his sulphur determinations he assigns to this body the formula $\left.\begin{matrix}\text{C H O}\\ \text{H}\end{matrix}\right\}$ S, naming it thioformic acid, and supposing it to be analogous to the thiacetic acid $\left.\begin{matrix}\text{C}_2\text{H}_3\text{O}\\ \text{H}\end{matrix}\right\}$ S of Kekulé.*

Seeing that the character of this interesting body has been but slightly investigated, I undertook, at the suggestion of Professor Roscoe, a further examination of its properties and the mode of its formation, the results of which, although mainly negative, I think it may be well to place on record.

When dry formic acid is acted on by pentasulphide of phosphorus, no trace of a sulphur acid is produced; the mixture distilled upwards continuously for several hours, slowly evolving sulphuretted hydrogen, the whole distillate boiling exactly at 101°C, and containing no sulphur in combination.

Heated in closed tubes to 106°C, the mixture underwent decomposition, but no thioformic acid was produced. So, likewise, when formic acid and pentasulphide of phosphorus were heated together under a total pressure of 3 atmospheres, torrents of sulphuretted hydrogen and carbonic oxide gases escaped, and the residual liquid all distilled over at 101°C, and contained no sulphur.

Formate of lead and pentasulphide of phosphorus distilled together, both in the dry and moist state, also yielded no thioformic acid.

From these experiments it is evident that thioformic acid cannot be produced by the method which Kekulé employed for the preparation of thiacetic acid. The elimination of sulphuretted hydrogen and carbonic oxide seems to point to a decomposition of the thioformic acid at the temperature of the experiments:

$$\text{Thus—}\left.\begin{matrix}\text{C H O}\\ \text{H}\end{matrix}\right\}\text{S} = \text{CO} + \left.\begin{matrix}\text{H}\\ \text{H}\end{matrix}\right\}\text{S}$$

By Limpricht's method of decomposing formate of lead at a high temperature with a current of sulphuretted hydrogen, a solid crystalline body was obtained; but it was produced in much smaller quantities than Limpricht states; 15 kilos. of formate yielding only about 3 grammes of the purified substance.

The body, which crystallizes in beautiful long white needles, was purified by repeated crystallizations from hot formic acid, and

* Ann. Ch. Pharm., xc, 309. Phil. Mag., [4] vii, 518.

dried completely in vacuo over sulphuric acid. The combustion of the substance was effected with chromate of lead in a long tube, the anterior part of which was not heated above low redness, according to the method lately described by Carius*, so that no peroxide of lead was required; and the water in the chloride-of-calcium-tube was found to be quite free from sulphurous acid. The sulphur was determined by oxidation with warm nitric acid; the sulphate of barium, being carefully rewashed with hydrochloric acid, and reweighed after incineration, to remove traces of nitrate of barium carried down.

The results were as follows—

Calculated for the formula $\left.\begin{matrix}C\,H\,O\\H\end{matrix}\right\}S$		Found.			
		(I.)	(II.)	(III.)	(IV.)
Carbon	19·3	27·93	29·25	28·21	
Hydrogen	3·2	4·70	4·83	5·23	
Sulphur	51·6	58·11	52·87	56·7	55·15
Oxygen	25·9				
	100·0				

Limpricht's numbers were—

Carbon	26·1	25·7	23·4
Hydrogen	5·6	4·7	6·3
Sulphur	51·2	52·5	
Oxygen			

From the foregoing analyses no definite formula can be deduced, in the absence of a vapour-density or accurate atomic weight determination, which the small quantity of the substance at my disposal unfortunately did not allow me to make. The analyses, however, show clearly that the body cannot be thioformic acid, as supposed by Limpricht, the excess of carbon over the theoretical quantity being too large to be explained by experimental error.

The purified substance, which showed under the microscope no trace of foreign bodies, but a perfectly homogeneous structure, crystallizes in white shining needles from solution in alcohol, ether, and acetic or formic acids, the alcoholic solution being neutral to litmus paper. The crystals melt at 120°C., and sublime unchanged at higher temperatures, depositing in long silky needles. The dry substance has a very slight odour, but its solution in formic acid has a strong penetrating sulphur smell.

* Ann. Ch. Pharm., cxvi, 1.

It is not acted on either by hot or cold hydrochloric acid, but is easily decomposed by nitric and sulphuric acids; it is also unacted on by solutions of carbonate or hydrate of potassium, and by sulphide of ammonium. The alcoholic solution gives no precipitate with chloride of barium, but with nitrate of silver a heavy white precipitate soluble in ammonia and boiling alcohol, is produced. I did not succeed in obtaining from this silver-salt any atomic weight from which a satisfactory formula for the body could be calculated.

XXXIX.—*On the Capacity of Arsenious Acid for Bases, and on certain Arsenites.*

By Charles L. Bloxam.

In the *Journal of the Chemical Society*, vol. xii, p. 177, and vol. xiv, p. 143, I have recorded some experiments which tend to prove that boracic and silicic acids are respectively tribasic and bibasic; but that, in consequence of their feeble acid character, at moderately elevated temperatures, their capacity for bases becomes fully manifested, only when these are presented to them either in the uncombined state, or in some form of combination in which they are held by very feeble ties.

The object proposed in the commencement of the experiments which I now submit to the Society, was to ascertain whether similar results would be obtained with another feeble acid, the arsenious, the capacity of which for bases did not appear to have yet been satisfactorily determined.

Starting from the same point as in the experiments upon boracic acid, I first examined the action of arsenious acid upon the alkaline carbonates at different temperatures.

Action of Arsenious Acid upon the Carbonates of Potassa and Soda at 212°F.

A quantitative examination of the substances employed having proved their purity, two sets of experiments were made with each

carbonate, in one of which, the acid, and in the other, the carbonate, was employed in excess.

When the arsenious acid was employed in excess, the experiment was conducted in the following manner. A weighed quantity of the alkaline carbonate was dissolved in water, the solution heated to 212°, and weighed quantities of arsenious acid added until the liquid refused to dissolve any more, even after long digestion*. It was then allowed to stand as long as any arsenious acid crystallised out, the clear liquid was evaporated to dryness on a water-bath, the residue dissolved in a very small quantity of water, and any undissolved arsenious acid (which was never in large quantity) added to that previously collected, and weighed after being dried at 212°†. By deducting the weight of this residual arsenious acid from that originally employed, the amount of acid which had combined with the alkali was ascertained. The alkaline arsenite was examined to prove that no carbonic acid had been retained, and that no arseniate of any consequence had been formed. The experiments were varied by using the opaque acid of commerce as well as that crystallised from hydrochloric acid, without affecting the results.

In those experiments in which the alkaline carbonate was employed in excess, the solution was evaporated to dryness on a water-bath, the residue dried at 212° until its weight was constant or nearly so, and the carbonic acid which it retained was determined in Fresenius and Will's apparatus. By deducting the weight of this carbonic acid from that known to be present in the alkaline carbonate employed, the amount of carbonic acid expelled by a given weight of arsenious acid was determined.

In stating the results, the equivalent of arsenious acid has been taken as = 99, that of carbonic acid = 22, of potassa = 47, and of soda = 31.

* Solutions of the alkaline arsenites dissolve free arsenious acid much more rapidly than water, and arsenite of potassa is superior in this respect to arsenite of soda.

† It had been determined by a preliminary experiment that the loss experienced by arsenious acid, when repeatedly moistened and dried at 212°, would have no influence on the result.

Action of Arsenious Acid in excess upon Carbonate of Potassa at 212°F.

One equivalent (69) of carbonate of potassa employed.

No.	Arsenious acid, in equivalents.	
	Employed.	Retained in combination.
1	10·00	1·94
2	9·50	2·00

The excess of arsenious acid left undissolved by carbonate of potassa appeared, when examined by the microscope, in right rhombic prisms, and similar crystals of arsenious acid were sometimes deposited as the alkaline solution cooled, though the crystals then obtained were more frequently octohedral*.

The solution of arsenite of potash, obtained in these experiments, slowly deposited beautiful rectangular prisms having the composition $KO.HO.2AsO_3 + Aq.$†, and losing one equivalent of water at 212°F. (Experiment gave 3·26 instead of 3·42 per cent. of water expelled at 212°.)

The salt was analysed by acidulating its solution with hydrochloric acid, precipitating the arsenic by hydrosulphuric acid, and evaporating the filtered solution to obtain the chloride of potassium.

The arsenite dried at 212° in a current of dry air gave the following results.

	Found.	Calculated.
KO	19·09	18·51
$2AsO_3$	77·35	77·95
HO	3·53	3·54
	99·97	100·00

In order to determine the constitutional water, the salt was gently heated over a spirit-lamp in a glass tube through which a current of dry air was passed, the water being collected in a weighed tube containing chloride of calcium. The salt fused, with separation of traces of metallic arsenic and arseniuretted hydrogen, into a clear

* The separation of prismatic crystals of arsenious acid from a solution in potash has been mentioned by Pasteur.

† The same salt was obtained by Pasteur, who saturated potash with arsenious acid, and added alcohol.

yellow liquid, which solidified on cooling to a very brilliant yellowish glass, extremely brittle and deliquescent*.

The analysis of this *vitreous arsenite of potash* established for it the formula $KO.2AsO_3$.

	Found.	Calculated.
KO	19·44	19·18
$2\,AsO_3$	79·76	80·82
	99·20	100·00

A little arsenic acid was found in the vitreous mass even when the fusion was effected in a stream of carbonic acid.

As a control for the above analysis of this salt, 67·46 grns. of the crystallised bi-arsenite ($KO.HO.2AsO_3 + Aq.$) were fused in a stream of dry carbonic acid, the water collected in a weighed tube containing chloride of calcium, and the gas then passed through bulbs filled with nitrate of silver to retain any arseniuretted hydrogen, of which a very slight trace only was detected. The water condensed in the drying-tube amounted to 4·57 grns. or 6·77 per cent. The loss suffered by the arsenite was 4·54 grns. The above formula for the crystallised salt requires a loss of 6·84 per cent. of water, exceeding by only 0·07 per cent. that found by experiment.

The vitreous arsenite of potash was also obtained (see exps. 16 and 17 in the Tables) by fusing carbonate of potash with an excess of arsenious acid.

Water dissolves the vitreous arsenite very readily, the solution gradually depositing crystals of the hydrated salt.

Strongly heated in a porcelain crucible, it emits copious vapours of metallic arsenic, and leaves an opaque mass of arseniate of potash.

The fused salt attacks platinum very readily, scraps of that metal being fused instantly when thrown into it, yielding a button of arsenide of platinum resembling grey cast-iron in character†. The abstraction of arsenic by the platinum had converted the arsenite into arseniate of potash. A little of the vitreous arsenite

* In the act of solidifying, this glass not only itself broke into several fragments, which were often projected with great force, but tore asunder any glass tube which contained it.

† The fused salt of the formula $KO.AsO_3$ had a similar effect upon platinum. 37·7 grains of this salt very easily effected the fusion of 42·8 grains of platinum at a red heat, the platinum having combined with 3·27 grns. of arsenic.

was heated in a hard glass tube to the softening point of the glass, without change, but on adding a few scraps of platinum, the salt was immediately converted into the arseniate.*

Action of Arsenious Acid upon an excess of Carbonate of Potassa at 212°F.

One equivalent (99) of arsenious acid employed.

No.	Carbonate of potassa employed. Eqs.	Carbonic acid expelled. Eqs.
3	1·00	0·75
4	1·00	0·82
5	1·00	0·74
6	0·86	0·64
7	0·66	0·66

It appears, therefore, that when carbonate of potassa is acted on by an excess of arsenious acid at 212°, one equivalent of potassa combines with two equivalents of the acid, and that, if the carbonate is in excess, one equivalent of arsenious acid combines with two-thirds of an equivalent of potassa.

On evaporating the solution, in this last case, to a small bulk, it deposited crystals of the acid arsenite ($KO.HO.2AsO_3+Aq.$), but, by evaporating to dryness at 212°, a mass of prismatic crystals was obtained, having the composition $2KO.3AsO_3+3HO$, which did not lose water by protracted exposure in the water-oven. The analysis of this salt gave the following numbers:—

	Found.	Calculated.
2KO	21·76	22·48
$3AsO_3$	72·04	71·05
3HO	6·35	6·47
	100·15	100·00

When moderately heated, the salt fused to a transparent vitreous mass.

Action of Arsenious Acid in excess upon Carbonate of Soda at 212°F.

One equivalent (53) of carbonate of soda employed.

No.	Arsenious acid, in equivalents.	
	Employed.	Retained in combination.
8	4·09	1·91
9	4·20	1·93
10	5·90	1·95

* Gehlen noticed that arsenious acid heated with platinum and carbonate of soda gives arsenide of platinum and arseniate of soda.

Action of Arsenious Acid upon an excess of Carbonate of Soda at 212°F.

One equivalent (99) of arsenious acid employed.

No.	Carbonate of soda employed. Eqs.	Carbonic acid expelled. Eqs.
11	2·00	0·69
12	1·00	0·67
13	1·00	0·69
14	1·00	0 66
15	0·66	0·66

The action of arsenious acid upon carbonate of soda at 212°F. is similar, therefore, to its action upon carbonate of potassa.

Neither of the solutions of arsenite of soda could be made to crystallise even after a great lapse of time. When the solution obtained with carbonate of soda and excess of arsenious acid was evaporated to dryness, and the residue dried at 212°, till of constant weight, it had the composition $NaO.2AsO_3$.

The solution of 3 eqs. of arsenious acid in 2 eqs. of carbonate of soda, when evaporated to a syrup on the water-bath, became black and assumed a peculiar metallic aspect, apparently from the separation of a minute quantity of finely divided metallic arsenic; it was kept for two months in this state, in an open basin, without change, but when diluted with water, after a short time it became colourless. Since long exposure *in vacuo* over sulphuric acid did not induce crystallisation, it was dried up, with great difficulty, on the water-bath, when it left a grey mass of confused prismatic crystals. After being dried at 212° till its weight became constant*, it was analysed with the following results:—

	Found.	Calculated.
$2NaO$	16·57	17·27
$3AsO_3$	83·40	82·73
	99·97	100·00

* During the drying of the alkaline arsenites, a faint alliaceous odour was generally observed, and nitrate of silver exposed on paper above the capsules became slightly blackened, indicating the evolution of a little arseniuretted hydrogen, produced by the decomposition of water, and attended with the formation of arsenic acid, traces of which were always discovered in the dry salts. A point was usually arrived at when the drying mass had assumed the consistence of honey, which it would retain even after long heating, until briskly stirred, when it became a very hard solid mass.

The salt was found to contain a very little arsenic acid, as might be expected from the separation of metallic arsenic mentioned above, arising probably from the splitting of a part of the arsenious acid ($5AsO_3 = 3AsO_5 + As_2$). The circumstance that so little arsenic acid was present is worth notice, since the syrupy arsenite had been exposed to the air for at least two months in a capsule covered with filter paper.

Action of Arsenious Acid upon the Carbonates of Potassa and Soda at a low red heat.

For these experiments, the heat of an Argand gas-burner was employed. Weighed quantities of arsenious acid and the alkaline carbonate were dissolved in water, in a porcelain crucible, the solution gently evaporated to dryness, and the residue gradually heated till its weight was constant. When an excess of arsenious acid was employed, the amount retained in combination by the alkali was ascertained by deducting the known weight of the latter from the total weight of the residue, previously tested for carbonic and arsenic acids. When the alkaline carbonate was in excess, the amount of carbonic acid expelled was inferred by deducting the weight of the residue, previously tested for arsenic acid, from the joint weights of the alkaline carbonate and arsenious acid, care being taken that the latter had not been volatilised during the experiment.

Action of Arsenious Acid in excess upon Carbonate of Potassa at a low red heat.

One equivalent (69) of carbonate of potassa employed.

No.	Arsenious acid, in equivalents.	
	Employed.	Retained in combination.
16	2·50	1·95
17	2·50	2·02

The product was a transparent glassy mass of $KO.2AsO_3$, having a dark colour, caused by the separation of a little arsenic in the metallic state.

Action of Arsenious Acid upon an excess of Carbonate of Potassa at a low red heat.

One equivalent (99) of arsenious acid employed.

No.	Carbonate of potassa employed. Eqs.	Carbonic acid expelled. Eqs.
18	1·00	1·09
19	1·00	1·05
20	1·00	1·04
21	1·25	1·06

It is evident, from these results, that an excess of arsenious acid acts upon carbonate of potassa, at a red heat, exactly as at 212°, but that the acid is capable of combining with one equivalent of potassa when heated to low redness with an excess of the carbonate.

Action of Arsenious Acid in excess upon Carbonate of Soda at a low red heat.

One equivalent (53) of carbonate of soda employed.

No.	Arsenious acid, in equivalents.	
	Employed.	Retained in combination.
22	2·5	1·97

The result of this experiment was a transparent vitreous mass of $NaO.2AsO_3$.

Action of Arsenious Acid upon an excess of Carbonate of Soda at a low red heat.

One equivalent (99) of arsenious acid employed.

No.	Carbonate of soda employed. Eqs.	Carbonic acid expelled. Eqs.
23	1·50	1·04

It appears, therefore, that, contrary to the expectations which I had been led to form by the behaviour of boracic and silicic acids, arsenious acid acts upon carbonate of soda in precisely the same manner as upon carbonate of potassa, both at 212°, and at a low red heat, and that the capacity of arsenious acid for bases of the formula MO, as measured by its action upon the alkaline carbonates, does not extend beyond one equivalent.

Action of Arsenious Acid upon the Hydrates of Potassa and Soda.

The experiments under this head were made in the same manner as those upon boracic and silicic acids described in the Society's Journal for July, 1861 (p. 143), the hydrates being fused in a silver tray, heated in a current of pure and dry air, until of constant weight, a known quantity of arsenious acid introduced, enough water added to nearly fill the tray, the whole then slowly evaporated to dryness in the current of air, and afterwards moderately heated over an Argand gas burner until no material loss of weight was perceptible.*

Action of Arsenious Acid upon Hydrate of Potassa at a low red heat.

One equivalent (99) of arsenious acid employed.

No.	Hydrate of Potassa employed. Eqs.	Water (HO=9) expelled. Eqs.
24	4·10	1·45
25	4·50	1·58
26	2·20	1·32

Action of Arsenious Acid upon Hydrate of Soda at a low red heat.

One equivalent (99) of arsenious acid employed.

No.	Hydrate of Soda employed. Eqs.	Water expelled. Eqs.
27	3·00	2·29
28	10·00	2·29
29	17·00	2·14
30	8·60	2·04

On examining the products of these experiments, a considerable quantity of arsenic acid was always detected, even when hydrogen, nitrogen, or coal-gas had been employed instead of atmospheric air, and it was proved by direct experiment, in an atmosphere of

* It had been determined, by a preliminary experiment, that the hydrates suffered no alteration in weight when dissolved in water and evaporated in this manner.

nitrogen, that when arsenious acid or an alkaline arsenite is fused with an excess of alkaline hydrate, an arseniate is formed, at the expense of the oxygen of the water, the hydrogen of which is disengaged, unaccompanied by arseniuretted hydrogen.

When a small excess of the alkaline hydrate was employed, one portion of the arsenious acid was oxidised at the expense of the remainder, metallic arsenic being disengaged.

Although, on account of these decompositions, no reliance can be placed upon this method for the determination of the capacity of arsenious acid for bases, it is interesting to observe that (as was found in the cases of boracic and silicic acids) the hydrate of soda is decomposed by arsenious acid to a greater extent than hydrate of potassa.

Having failed hitherto to obtain any conclusive evidence as to the capacity of arsenious acid for bases, I next proceeded to determine the composition of such of the arsenites as appeared most likely to aid in solving the question.

Arsenite of Silver.

The formula of the yellow arsenite of silver has been given by Pasteur as $2AgO.AsO_3$ and by Filhol as $3AgO.AsO_3$.

Believing that the discrepancy was caused by the tendency of the precipitate to carry down adhering arsenious acid, I dissolved a weighed amount of pure bi-arsenite of potash ($KO.HO.2AsO_3$) in so much water that no arsenious acid was separated when a portion of the solution was acidulated with nitric acid and set aside. A measured quantity of the alkaline solution was then tested with a standard solution of nitrate of silver, added as long as any precipitate was produced. Each equivalent of the arsenite was found to require 1·5 eqs. of nitrate of silver.

The yellow precipitate, which was at first very bulky, but became crystalline on standing, and strongly adherent to the lines made by the stirring-rod, was washed and dried at 212°. It appeared in tufts of needles under the microscope.

For the analysis of this precipitate, it was oxidised by nitric acid, the silver precipitated by hydro-chloric acid, and the arsenic acid in the filtrate determined as arseniate of magnesia and ammonia. The results were—

Oxide of silver*	..	.. 74·77 per cent.
Arsenious acid	..	.. 25·88 „

Since the formula $2AgO.AsO_3$ would require only 70·9 per cent. of oxide of silver, and the liquid from which the precipitate had separated was decidedly acid, it appears highly probable that the precipitate was a mixture of $3AgO.AsO_3$ with an excess of arsenious acid.

The decomposition of the bi-arsenite of potassa by nitrate of silver would therefore be represented by the equation.

$$2(KO.HO.2AsO_3) + 3(AgO.NO_5) = 3AgO.AsO_3 + 2(KO.NO_5) + HO.NO_5 + 3AsO_3 + HO.$$

The filtrate from this precipitate was mixed with more nitrate of silver, and carefully neutralised with ammonia. A fresh precipitate, similar to the preceding, was obtained. Dried at 212°F., it was found to contain 22·19 per cent. of arsenious acid, the formula $3\,AgO.AsO_3$ requiring 22·15.

The sesquiarsenite of soda ($2NaO.3AsO_3$) was found to require 2 eqs. of nitrate of silver for complete precipitation, yielding a precipitate of $3\,AgO.AsO_3$, and a very feebly acid solution.

$$3(2NaO.3AsO_3) + 6(AgO.NO_5) = 2(3AgO.AsO_3) + 7AsO_3 + 6(NaO.NO_5).$$

Arsenites of Lead.

Two arsenites of lead were analysed by Berzelius, viz., $PbO.AsO_3$ obtained by saturating ammonia with arsenious acid, and precipitating by neutral acetate of lead, and $2PbO.AsO_3$ prepared in a similar manner with tribasic acetate of lead. I dissolved one equivalent of acetate of lead in water, mixed the solution with ammonia in excess, and added it to an aqueous solution of half an equivalent of arsenious acid.

The precipitate was well washed, dried at 212°, and analysed by oxidising it with nitric acid, precipitating the lead as sulphate, and the arsenic as arseniate of magnesia and ammonia.

* Ag=108.

	Found.	Calculated.
2PbO*	68·39	69·28
AsO_3	31·43	30·72
	99·82	100·00

Another arsenite of lead was prepared by precipitating a dilute solution of bi-arsenite of potassa (I) or of sesquiarsenite of soda (II) by nitrate of lead.

The precipitates, dried at 212° till of constant weight, gave the following results on analysis.

	Found.		Calculated.
	I.	II.	
3PbO	60·81	60·72	59·80
$2AsO_3$	34·70	34·45	35·36
3HO (by difference)	4·49	4·83	4·84
	100·00	100·00	100·00

I am disposed to believe that this salt $3PbO.3HO.2AsO_3$ is formed upon the tribasic type 2 ($3MO.AsO_3$), having three atoms of water in the place of fixed base.

Arsenite of Copper.

The precipitates of arsenite of copper were analysed by oxidising them with nitric acid, precipitating the arsenic acid as arseniate of magnesia and ammonia, acidulating the filtrate with hydrochloric acid, and precipitating the copper either by hydrosulphuric acid or by hyposulphite of soda. The result was controlled by determining the arsenious acid volumetrically with a standard solution of permanganate of potash.

By mixing a dilute solution of the biarsenite of potash ($KO.HO.2AsO_3$) with sulphate of copper as long as any precipitate was formed, a decidedly acid filtrate was obtained, and the precipitate, when dried at 212°, was found to contain

Oxide of copper†	1·88 eqs.
Arsenious acid	1·00 „
Water	1·16 „

* Pb=103·6.
† Cu=31·7.

The composition of this precipitate rendered it probable that, like the arsenite of silver, it had carried down an excess of arsenious acid, and that its true formula should be $2\,CuO.HO.AsO_3$.

On adding more sulphate of copper to the liquid filtered from this precipitate, and carefully neutralising with ammonia, a further precipitate was obtained, which was found, after drying at 212°, to contain

Oxide of copper	2·21 eqs.
Arsenious acid.. ..	1·00 „
Water	1·26 „

so that it was probably the same salt ($2\,CuO.HO.AsO_3$) which had now carried down an excess of hydrated oxide of copper.

The precipitate obtained from sesquiarsenite of soda ($2NaO.3AsO_3$) and sulphate of copper, when dried at 212°, contained

Oxide of copper	2·35 eqs.
Arsenious acid.. ..	1·00 „
Water	0·92* „

By mixing an aqueous solution of arsenious acid with ammonio-sulphate of copper, a precipitate was obtained which, when dried in air till of constant weight, contained

Oxide of copper	2·02 eqs.
Arsenious acid	1·00 „
Water	2·89 „

After drying *in vacuo* over sulphuric acid, it gave

	Found.	Calculated.
$2CuO$	42·69	42·40
AsO_3	52·67	52·80
HO (by difference)	4·64	4·80
	100·00	100·00

Admitting the water to play the part of a base, the arsenite of copper is formed upon the tribasic type.

* Scheele's prescription for the commercial green arsenite of copper involves 2·3 eqs. of oxide of copper for 1 eq. of arsenious acid, so that Scheele's green, dried at 212°, appears to be essentially a mixture of $2CuO.HO.AsO_3$ with an excess of oxide of copper.

Arsenite of Baryta.

When a solution of arsenious acid in ammonia was precipitated by chloride of barium, a gelatinous semi-transparent precipitate was obtained, which was dissolved to a very considerable extent by water (yielding an alkaline solution), was dried with great difficulty, and absorbed carbonic acid from the air, so that it was very unfit for accurate analysis.

However, it was dried at 212°, dissolved in hydrochloric acid, the baryta precipitated as sulphate, and the arsenious acid determined in the filtrate by precipitation with hydrosulphuric acid. It gave

Baryta*	.. ..	1·00 eqs.
Arsenious acid	.. ..	0·87 „
Water	.. ..	1·93 „

Another specimen, prepared by decomposing a solution of sesquiarsenite of soda ($2NaO.3AsO_3$) with two equivalents of chloride of barium, gave, when dried at 212°,

Baryta	.. ..	1·00 eqs.
Arsenious acid	.. ..	1·21 „
Water	.. ..	1·96 „

The salt prepared by this method would probably have carried down with it an excess of arsenious acid, whilst that first prepared had retained some carbonate of baryta.

I did not succeed in obtaining a more satisfactory specimen of this salt, but if it be allowable to take the mean of the above results

Baryta	.. ..	1·00 eqs.
Arsenious acid	.. ..	1·04 „
Water	.. ..	1·94 „

the formula of the arsenite of baryta dried at 212°, would be $BaO.2HO.AsO_3$.

Arsenite of Magnesia.

A cold saturated solution of arsenious acid is not precipitated by sulphate of magnesia, but a mixture of this salt with chloride

* Ba = 68·5.

of ammonium and ammonia throws down a white pulverulent amorphous precipitate which does not contain ammonia.

A solution of 1 part of arsenious acid in 150 parts of water gave an abundant precipitate with the ammoniacal magnesia solution, on stirring, and even when 700 parts of water were present, the precipitate was obtained after a few minutes, which renders it necessary to be cautious in the employment of the magnesia test for arsenic and phosphoric acids when arsenious acid is present in the liquid.

In order to determine the composition of the arsenite of magnesia, it was dissolved in nitric acid, which oxidised it with great violence, even without the application of heat, and the solution mixed with chloride of ammonium and excess of ammonia, which precipitated the whole of the arsenic and magnesia as arseniate of magnesia and ammonia, from the weight of which those of the magnesia and arsenious acid were deduced. The water was determined directly by heating the salt in a current of dry air, and collecting the water in a tube filled with chloride of calcium.

The result of the analysis was confirmed by determining the arsenious acid with a standard solution of permanganate of potash.

Dried at 212° F.

	Found.	Calculated.
2MgO*	25·63	25·48
AsO_3	63·44	63·06
2HO	10·73	11·46
	99·80	100·00

Dried at 400° F.

	Found.	Calculated.
2MgO	26·93	27·03
AsO_3	66·66	66·89
HO†	5·07	6·08
	98·66	100·00

* Mg=12.

† Had the water been determined by difference, it would have amounted to 6·41 per cent. It was, of course, difficult to determine the water exactly in such a salt at so high a temperature.

Dried above 400° F.

	Found.	Calculated.
$2MgO$	28·29	28·78
AsO_3	70·04	71·22
	98·33*	100·00

The composition of the arsenite of magnesia dried below 400° F. ($2MgO.HO.AsO_3$) also supports the tribasic character of arsenious acid.

Arsenite of Zinc.

This salt, which was the most remarkable and definite of the precipitated arsenites, was prepared in the following manner:

Solution of sulphate of zinc was mixed with ammonia till the greater part of the precipitate had re-dissolved; a considerable quantity of chloride of ammonium was then added, the solution filtered, and mixed with an excess of a cold saturated solution of arsenious acid. A white bulky precipitate was thus obtained, which shrank excessively on standing, and exhibited the character possessed by crystalline precipitates of adhering very strongly to the lines made by the stirring-rod. When examined under the microscope, however, it was found to consist of very beautiful semi-transparent globules, in most cases so perfectly spherical that it was difficult to prevent them from rolling about on the microscope-slide, where they had much the appearance of some farinaceous substance.

When dried at 212°, this arsenite of zinc became a glistening pearly powder. The analysis of this specimen precipitated from the strongly alkaline solution is given as I in the following Table.

The filtrate from this precipitate was partly neutralised with sulphuric acid, when a fresh precipitate of the same character was obtained, the analysis of which is given under II.

On further neutralising with sulphuric acid, opaque globules were obtained, which proved, on analysis, to contain an excess of arsenious acid.

The arsenite of zinc was analysed by dissolving it in hydrochloric acid, precipitating the arsenious acid by hydrosulphuric acid, evaporating the solution, and precipitating the oxide of zinc

* A little water was still retained.